



Mechanism of mercury vapor release from flue gas desulfurization gypsum



Zhen-Wu Zhu, Yu-Qun Zhuo*, Ya-Ming Fan, Zhi-Peng Wang

Key Laboratory for Thermal Science and Power Engineering, Ministry of Education, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:

Received 9 May 2016

Received in revised form 21 September 2016

Accepted 10 October 2016

Available online 17 October 2016

Keywords:

Mercury vapor release

FGD gypsum

Temperature

UV radiation

Moisture content

ABSTRACT

Wet flue gas desulfurization (FGD) systems designed to remove sulfur dioxide can capture soluble oxidized mercury which then lead to mercury accumulation in FGD gypsum. In this study, the mercury species in three FGD gypsum samples were first determined using a temperature programmed decomposition method. The mercury species in the FGD gypsum was mainly HgS. Mercury vapor release to the atmosphere from FGD gypsum was then investigated. The effects of temperature, UV radiation and solid moisture content on mercury release were studied in controlled laboratory experiments. Detectable amounts of mercury were constantly emitted from three samples. The mercury release rates in the dark at room temperature were found to vary from 0.31% to 2.65% during the 180-day period tests. The temperature, UV radiation and solid moisture content all significantly enhanced the mercury release from the FGD gypsum with synergistic enhancements existing between the temperature/UV radiation and the solid moisture content. The promotion of oxidized mercury reduction and Hg⁰ desorption and diffusion might be the reasons for the enhancement of mercury release by these factors. Considering the temperature, UV radiation and solid moisture content fluctuations of FGD gypsum when exposed to natural environment, the mercury release from FGD gypsum disposed outdoor might be significant.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Mercury (Hg) is highly toxic and can be enriched through food chain which can lead to various diseases. Elemental mercury (Hg⁰) can enter into global atmospheric circulation and be transported over large distances before being deposited to soils and surface waters. This makes Hg emission to be a global environmental issue that is attracting more and more attention. Coal-fired power plants have been shown to be one of the largest anthropogenic point sources of atmospheric mercury [1,2]. China is the largest coal consumption country in the world and the total Hg emission from coal-fired power plants in China was about 132 tons in 2007 [3].

Wet flue gas desulfurization (FGD) systems, which are designed to control the release of sulfur dioxide, have been demonstrated to effectively capture soluble oxidized mercury (Hg²⁺) compounds [4,5]. The Hg captured is mainly retained in the FGD gypsum byproduct after dehydration [6,7]. Consequently, a considerable amount of Hg is bound to the FGD gypsum. This is especially true after halogen addition technology has been applied which will promote the oxidization of Hg⁰ in the flue gas [8]. Hao et al. [9] studied FGD gypsum samples from 70 coal-fired power plants in 20 provinces in China and the results showed that the Hg concentrations in FGD gypsum ranged from not detectable to 4330 ± 620 µg/kg. Now FGD gypsum is not classified as hazardous

waste in China and many other countries. There is no strict control on the transportation, reuse and storage of FGD gypsum. FGD gypsum has been regarded as an alternate of natural gypsum and been applied for several beneficial purposes both in China and many other countries. According to the American Coal Ash Association annual report, the production of FGD gypsum was about 24,400,000 tons in 2013 in American with 36% of the total production used in encapsulated applications such as cement, concrete and wallboard production, while 12.8% was used in non-encapsulated applications such as structural fills/embankments, agricultural, soil stabilization and mining reclamation [10]. And the remaining 52% was disposed as waste material in industrial landfills. About 52 million tons of FGD gypsum was produced in 2012 in China with 56% being used in beneficial applications such as wallboard production, agricultural soil reclamation and cement additives [9]. The remaining FGD gypsum would mainly end up in landfills or outdoor storage due to the lack of downstream industrial users. And this is especially common in less developed area of China.

The Hg reactions in gypsum slurries in wet FGD systems are rather complicated with some of the absorbed Hg²⁺ in the slurry reduced by the sulfite ions and release as Hg⁰ [11,12]. Previous studies on soil have shown that Hg can cycle between adsorption and desorption among air-solid interfaces and background soil has been regarded as an important source to the global Hg cycle [13]. Hg released from the soil is mainly in form as Hg⁰ through complex physical, chemical and biological processes [14]. The organic matter in soil plays an important role in both abiotic and biotic processes that control the Hg release

* Corresponding author.

E-mail address: zhuoyq@tsinghua.edu.cn (Y.-Q. Zhuo).

from soil [15]. Temperature, UV radiation and soil moisture content have also been found to be important parameters that influence Hg release from soil [16–19].

Concentrations of Hg may be higher in FGD gypsum compared to natural soil. Similarly, Hg retained in the FGD gypsum may also have the potential to release as Hg⁰. Some research works have revealed the volatilization of Hg⁰ from FGD gypsum [20–22]. However, the mechanisms of the Hg vapor release from FGD gypsum remain unclear. Unlike soil, Hg in FGD gypsum is mainly in the form as inorganic mercury species and FGD gypsum nearly contains no organic matters which have high affinity with mercury compounds and participate in the reactions related to Hg release from soil. The different material chemistry and Hg species in FGD gypsum suggest that the Hg vapor release from FGD gypsum may be different from that in soil. FGD gypsum would be in contact with the natural environment in the non-encapsulated applications such as agricultural practice and soil stabilization. The FGD gypsum applied for encapsulated applications such as wallboard and cement may also be affected by the changes of temperature and humidity of natural environment. And the large amounts of FGD gypsum that ended up in landfills or outdoor storage without any beneficial applications would also be exposed to outdoor environment. Because of current management scenarios of FGD gypsum, a large proportion of FGD gypsum would have the opportunity to be exposed to natural environment. The temperature, UV radiation and solid moisture content might also affect the Hg release from FGD gypsum as that occurs in soil. Therefore, it is necessary to study the influence of these natural environmental conditions on Hg release from FGD gypsum. Considering the huge amounts of FGD gypsum generated every year in China and many other countries, the Hg release from FGD gypsum may not be negligible.

The emphasis of this study was to investigate the Hg vapor release characteristics from FGD gypsum. The effects of temperature, UV radiation and solid moisture content on the Hg release were studied in laboratory experiments. The Hg speciation in FGD gypsum was analyzed to evaluate the Hg release mechanism with the aim to comprehensively address the physicochemical processes controlling the Hg release from FGD gypsum.

2. Materials and methods

2.1. Sampling and characterization

Samples of FGD gypsum labeled as CQ, LYG and EZ were obtained from three different coal-fired power plants in China. The samples were collected from fresh FGD gypsum and stored in sealed glass bottles at 4 °C until testing. The moisture contents of CQ, LYG and EZ samples were 13.68%, 8.95% and 25.55%, respectively. As listed in Table 1, the coal types of the three coal-fired power plants included bituminous, lignite and anthracite, representing all the major coal types burned in Chinese power plants. All the tested power plants were equipped with selective catalytic reduction (SCR), electrostatic precipitator (ESP) and wet FGD system to control the emissions of NO_x, particulate matter and SO₂.

The Hg contents in the samples were determined using a Lumex RA-915M + PYRO-915 (Lumex, Russia) which can achieve direct measurement of Hg in solid matrix. The contents of the other elements were determined by inductively coupled plasma mass spectrometry (ICP-MS, ThermoFisher X series II, German) after microwave digestion. The whole procedure followed US EPA Method 3052. X-ray diffraction

(XRD, D/Max-2500 pc, Rigaku Inc., Japan) analysis of air-dried samples was used to identify the basic crystalline phase. The structure and morphology of each sample was also examined by scanning electron microscopy (SEM, S-5500, Hitachi, Japan).

2.2. Mercury release measurement

The Hg release from FGD gypsum was measured in the system as shown in Fig. 1. 40 g of FGD gypsum sample (as received) was placed in a clean quartz glass chamber of 1000 ml. Ambient air scrubbed of ambient mercury by activated carbon was slowly introduced into the chamber at the rate of 1 l/min. Any Hg release from the FGD gypsum was then carried out of the chamber and captured by the activated carbon trap at the exit. The Hg content in the activated carbon trap was then measured by Lumex 915M + PYRO-915 to determine the Hg release rate from FGD gypsum. The Hg release rate was the ratio of Hg release content to the total Hg content in the tested FGD gypsum samples. To investigate the impact of temperature and UV radiation, the Hg release experiments were conducted in parallel at three different conditions. The first batch of samples was placed in the dark without UV light at room temperature (maintained 25 ± 3 °C during the 180-day period of experiment). The second batch of samples was placed in light at room temperature to study the influence of UV light. The light was generated by a UV tube (340 nm, 40 W) which could mimic the ultraviolet region of solar radiation. The third batch of samples was placed in the dark in an oven with the temperature maintained at 50 °C to study the influence of temperature. The activated carbon traps were replaced and had their Hg contents measured in every 30 days, while the Hg release content was also recorded in every 2 days during the initial 10 days of the experiment. The release experiment lasted for 180 days to study the long-term release characteristics of Hg. The impact of solid moisture content was investigated by adding 5 ml deionized water to every sample homogeneously each time after the 180 days of continuous observation. The water additions were conducted three times. The experiments about the impact of solid moisture content lasted for 20 days and the Hg release content was recorded in every 2 days. The content of Hg release in the first 2 days before water addition was measured at the beginning. Then 5 ml water was added and the Hg release was measured along with the change of solid moisture content determined by weighing the chamber every 2 days in the following 8 days, so as to mimic the wetting and drying process of FGD gypsum in natural environment. The water was then added at the end of 10th day and 14th day in the experiments to confirm the effect of water addition and also to study the Hg release characteristic in the successive wetting events. All the experiments were conducted in triplicate to verify the data reliability with the mean values used.

3. Results and discussion

3.1. Characterization of FGD gypsum

The mineralogy characterization of the FGD gypsum samples were studied by XRD analysis. As shown in Fig. 2, calcium sulfate dehydrate was the predominant crystalline phase in all the samples. This meant that most of the calcium sulfite (CaSO₃) had been transformed to calcium sulfate (CaSO₄) by the forced-oxidation process in the wet FGD system. There were also minor amounts of calcite and quartz in the

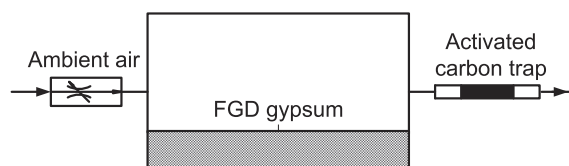


Fig. 1. Mercury release measurement system.

Table 1
General information of the tested power plants.

Sample	Coal type	Air pollution control devices	Installed capacity (MW)
CQ	Lignite	SCR + ESP + wet FGD	300
LYG	Bituminous	SCR + ESP + wet FGD	1000
EZ	Anthracite	SCR + ESP + wet FGD	330

Download English Version:

<https://daneshyari.com/en/article/6476713>

Download Persian Version:

<https://daneshyari.com/article/6476713>

[Daneshyari.com](https://daneshyari.com)